See also: **II/Chromatography: Liquid:** Derivatization; Mechanisms: Ion Chromatography.

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Thin-Layer (Planar) Chromatography

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Introduction

Thin-layer chromatography (TLC) is a subdivision of liquid chromatography in which the mobile phase (a liquid) migrates through the stationary phase (thin layer of porous sorbent on a flat inert surface) by capillary action. In 1938, two Russian workers, Izmailov and Schraiber, separated certain medicinal compounds on binder-free horizontal thin layers of alumina spread on a glass plate. Since the development was carried out by placing solvent drops on the glass plate containing sample and sorbent, their method was called drop chromatography. This method remained unnoticed for 10 years until two American chemists, Meinhard and Hall, used a mixture of aluminium oxide (adsorbent) and celite (binder) in a layer on a microscope slide to separate Fe^{2+} from Zn^{2+}. They called this technique surface chromatography and this was the first application of planar chromatography to the separation of inorganic ions. The real impetus for advancement of TLC started in 1951 with the work of Kirchner and his associates. Stahl introduced the term thin-layer chromatography in 1958 and standardized procedures, materials and nomenclature. The rapid growth of TLC slowed down during the 1970s with the rise in popularity of high performance liquid chromatography (HPLC) and ion chromatography (IC). However, recent improvements in TLC have removed many of its limitations.

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High performance TLC (HPTLC) layers, being thinner and made of more uniform particle size sorbents, provide faster separations, reduced zone diffusion, lower detection limits, less solvent consumption and better separation efficiency. The distinct advantages of TLC over HPLC have been identified as low solvent consumption, low operational cost, easier sample preparation, more rapid throughput, greater detection possibilities and the use of disposable plates. TLC permits the simultaneous analysis of many samples in the same time required for one HPLC analysis and samples and standards are analysed by TLC under exactly the same conditions rather than serially, as in HPLC. Typically, 18–36 samples can be run on a single HPTLC plate with a development time of 3–20 min over a migration distance of 2–7 cm. However, the influence of environmental conditions on the reproducibility of R_F values and poor separation efficiency have been major disadvantages of TLC compared with HPLC and gas chromatography (GC).

TLC can be used for *qualitative* analysis, to identify the presence or absence of a particular substance in a mixture; *quantitative* analysis, to determine precisely and accurately the amount of a particular substance in a sample mixture; and *preparative* analysis, to purify and isolate a particular substance for subsequent use. All three applications require the common procedures of sample application, chromatographic separation and component visualization. However, analytical TLC differs from preparative TLC in that volumes and/or weights of samples are applied to thicker layers in the latter case.

Inorganic TLC

Though the first published reports on TLC described the separation of inorganic species, the importance of inorganic TLC did not receive recognition until the beginning of the 1960s when Seiler separated inorganic substances. After the work of Seiler, TLC of metal ions received a great impetus. Some of the major fields in which inorganic TLC has found applications include the analysis of biological, food, geological, industrial, pharmaceutical, soil, water and industrial waste water samples. The purpose of this article is to present briefly the current state-of-the-art procedures of TLC/HPTLC as applied to the analysis of inorganic ions.

Procedure

TLC is an offline process in which various steps are carried out independently (**Figure 1**). The basic TLC procedure involves the spotting of sample mixture (5–10 μL for conventional TLC and 1–2 μL for HPTLC) at about 1.5–2 cm above the lower edge of the layer, drying the spot completely at room temperature or at an elevated temperature, development of the plate, usually by one-dimensional ascending technique in a closed chamber (cylindrical or rectangular) to a distance of 8–10 cm, removing the plate from the developing chamber, removal of mobile phase from the layer by drying, detection of spots on the plate using a suitable detection reagent/procedure, measurement of R_F values of resolved spots and determination of the separated analyte. The differential migration of components in a mixture is due to varying degrees of affinity of the components for the stationary and mobile phases.

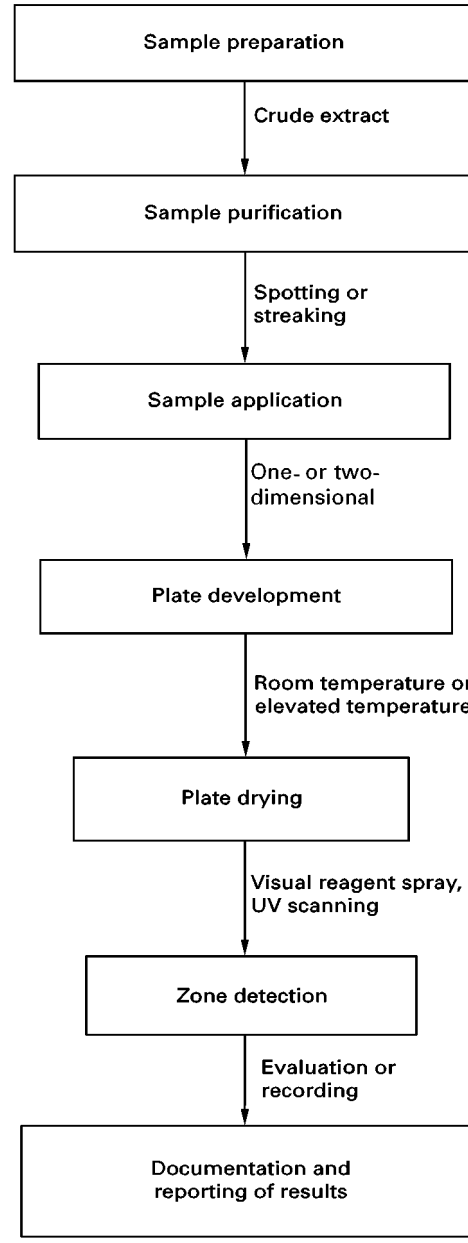

Figure 1 Schematic diagram showing the steps involved in a TLC process.

Sample Preparation

The sample solution to be analysed must be sufficiently concentrated to provide clear detection and/or be pure enough so that it can be separated as a discrete and compact zone. For low concentrations of analyte in a complex sample, preconcentration and clean-up procedures must frequently precede TLC.

Metal solutions are generally prepared by dissolving their corresponding salts in distilled water or 0.1 mol L^{-1} HCl (or HNO_3) to a final metal concentration of 0.1–0.2 mol L^{-1}. Rare earth oxide solutions are prepared by fusion followed by dissolution in 0.5–6 mol L^{-1} HNO_3 and anion solutions in distilled water, dilute acid or alkali are prepared from sodium, potassium and ammonium salts of the corresponding acids. Metal complexes are used as freshly prepared solutions in ethanol, acetone, chloroform or distilled water. Specific standard methods are followed for sample preparation to identify and determine metal ions in biological, environmental, alloys, plants, foods, textile and geological samples.

TLC Plate Preparation

The current trend is to use commercially available pre-coated plates. The manual preparation of layers involves the coating of a slurry of the adsorbent (silica

gel, alumina, etc.) on to glass, aluminium or plastic sheets (20×20 or 20×10 cm) with the help of an applicator. The thickness of the dried layer of analytical purposes is kept to 0.1–0.3 mm. A binder (starch, gypsum, dextrin, polyvinyl alcohol) is usually added to the adsorbent to provide better adhesion, mechanical stability and durability. The addition of a fluorescent indicator compound is optional. Compared to conventional TLC, HPTLC layers are produced from sorbents of smaller and more uniform particle size (5–10 μm instead of 10–20 μm).

Sample Application

Definite volumes of samples are applied as spots or streaks using a micropipette, microsyringe or glass capillaries. A number of automatic spotters of various designs are available for sample application. The nano-applicator (Nanomat) is an example of a micrometer-controlled syringe which has a dynamic volume range of 50–230 nL. Another applicator (Linomat) allows sample application in narrow bands by a spray-on technique. The application of a sample as a streak or band provides more efficient separations because the efficiency of the separation on a TLC plate depends on the diameter of the spot along the direction of development. Thus, the best efficiency is achieved with the smallest diameter spot. Alternatively, the use of TLC plates with concentration zones converts the sample from the original spot into a band or streak. These plates consist of a bottom layer (2–2.5 cm) of a chromatographically inactive adsorbent (e.g. Kieselguhr) followed by the layer of an active adsorbent (silica or bonded silica). The advantages of sample application as a streak and the use of TLC plates with concentration zones are illustrated in **Figure 2**. The general aspects of a sample application have been reviewed by Jaenchen.

Development Techniques

The migration of the mobile phases through the stationary phase (or sorbent layer) to effect separation of samples is called development. One-dimensional ascending development is the most commonly used mode in inorganic TLC. Other development techniques, such as multiple, stepwise, circular and two-dimensional development, have also been used to a limited extent. The migration distance for the mobile phase is kept to 10–12 cm for conventional TLC and 2–6 cm for HPTLC. Dzido has described the variants of the development techniques.

Chromatographic Systems

A combination of stationary and mobile phases constitutes a chromatographic system. The proper selection of stationary and mobile-phase conditions determines the effectiveness of a separation.

Stationary Phase (Layer Sorbent)

Many materials have been used as stationary phase in inorganic TLC but silica gel, an amorphous and porous adsorbent, has been the most favoured material, followed by alumina and cellulose. Thin layers of silica gel G (gypsum binder) and S (starch binder) with or without fluorescent indicator are frequently used. Silica gel is slightly acidic in nature and the silanol groups (Si–OH) can interact with solute molecules. On the other hand, alumina (aluminium oxide) is basic and more reactive than silica gel. Adsorption is the separation mechanism with both alumina

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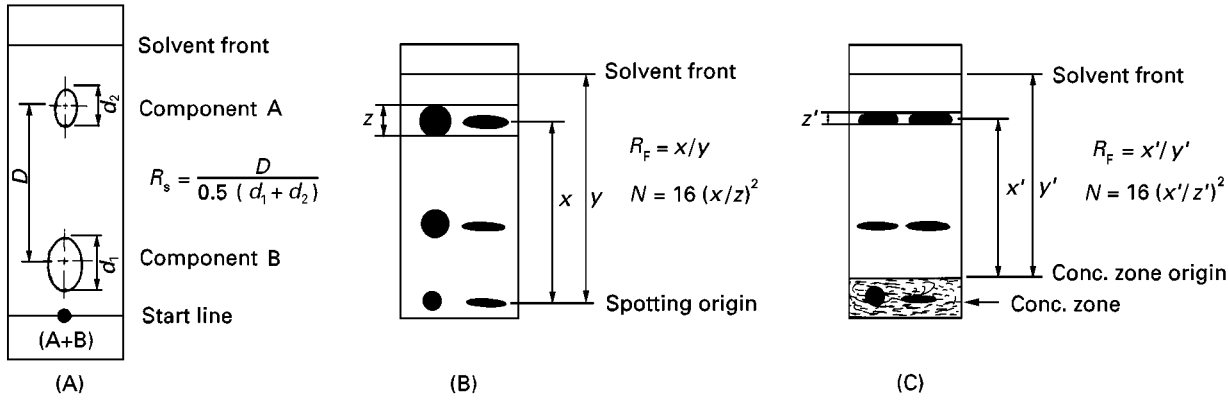

Figure 2 (A) Resolution of a two-component mixture on a TLC plate; (B) improved efficiency due to streaking; and (C) utility of concentration zone as a promoter of efficiency.

and silica gel. Cellulose, an organic material, is used as a sorbent to perform separations with increased sensitivity of detection and decreased development time compared to paper chromatography. The various layer materials may be broadly classified as:

1. nonsurface-modified or untreated sorbents;
2. impregnated or treated sorbents (organic and inorganic impregnants);
3. bonded or chemically modified sorbents (hydrophobic modified or reversed-phase and hydrophilic modified);
4. inorganic ion exchangers;
5. mixed sorbents.

More detailed information on pre-coated layers and sorbents that are commonly used in TLC is available elsewhere (see Further Reading).

The selective aplication of these different types of layer materials in inorganic TLC is summarized below.

Anions Silica gel, silica gel silica impregnated with fluorescein or inorganic salts, silica gel + antimonic acid/alumina/hydrous antimony(V) oxide/Zr(IV) molybdate, Sephadex, microcrystalline cellulose, surface-modified cellulose, cellulose + Kieselguhr/alumina, Kieselguhr, alumina, kaolin, hydrated stannic oxide and polyamide have all been used for the separation of anions.

Metal ions and rare earth elements The various layer materials used for the separation of metal ions, metal complexes and rare earth elements (REE) may, broadly, be classified as follows.

Nonsurface modified or untreated sorbents These include silica gel, alumina, cellulose, polyamide, polyacrylonitrile, Sephadex and Kieselguhr. Layers of chitin and its deacetylated derivative chitosan have been used to separate metal ions.

Impregnated or treated sorbents In general, silica gel impregnated with aqueous salt solutions, high molecular weight amines, organophosphorous compounds and organic chelating agents has been widely used for the separation of metal ions and REE. Metal complexes have been separated on silica gel impregnated with chlorobenzene, *p*-toluidine or surfactants and on layers of egg shell powder impregnated with Triton X-100.

Bonded or chemically modified sorbents Lipophilic C_{18}-bonded silica gel for REE and metal complexes, aminopropyl silica gel (NH_2) and octadecyl silica gel (C_{18}) for lanthanide complexes of tetraphenyl porphine and surface-modified cellulose as well as cellulose derivatives for several metal ions have been used.

Mixed sorbents Combinations of silica gel and microcrystalline cellulose for noble metal ions and transition metal chlorosulfates, silica gel and microcrystalline cellulose containing ammonium nitrate for REE and silica gel and inorganic ion exchange gel mixtures for transition metal ions have been used.

Other sorbents Synthetic inorganic ion exchangers, porous glass sheets, soil and soil–flyash mixture, polychrome A, carbamide–formaldehyde copolymer and immobilized analogue of dibenzo-18-crown-6 on silica support for metal ions and diatomite for REE have also been used, but to a lesser extent.

The adsorbents in different forms (untreated, impregnated, chemically modified or mixed) preferred in the analysis of inorganic ions since 1973 are shown in **Table 1**.

Anions Silica gel > cellulose > alumina > inorganic ion exchangers > Kieselguhr > polyamide.

Cations/metal ions Silica gel > cellulose > inorganic ion exchangers > alumina > chitin and chitosan > diatomite > soil.

Metal complexes Silica gel > alumina > cellulose > polyacrylonitrile > Sephadex = polyamide.

The salting-out efficiency of mixed aminocarboxylato Co(III) complexes obtained on different adsorbents shows the sorbent precipitation in the order (with small discrepancies) polyacrylonitrile > cellulose > silica gel. Polyacrylonitrile is the most suitable sorbent for the separation of complexes. The HPTLC results of rare earth–tetraphenylporphine complexes show an increase in R_F values in the order of the atomic number on NH_2-bonded silica plates and a reverse trend, i.e. decrease in R_F values, with an

Table 1 Number of publications (%) on some sorbent layers appearing from 1973 to 1996

Layer material	*Per cent publications*		
	Metal ions	*Metal complexes*	*Anions*
Silica gel	49.6	75.6	50.5
Alumina	6.4	10.7	9.3
Cellulose	29.3	4.8	29.3
Inorganic ion exchanger	10.0		4.0
Chitin and chitosan	2.0		
Polyacrylonitrile		4.8	
Polyamide		~1.0	1.3

increase in atomic number is obtained on C_{18}-bonded silica layers.

Mobile Phase (Solvent System)

With a particular sorbent layer, the separation possibility of a complex mixture is greatly improved by the proper selection of the mobile phase. Mixtures of organic solvents containing an aqueous acid, base or a buffer are, in general, well suited for the separation of ionic species whereas anhydrous organic solvents are more useful for separating nonionic species. The following mobile phases have been used for inorganic TLC.

Inorganic solvents This includes solutions of mineral acids, bases, salts and mixtures of acids, bases and/or their salts.

Organic solvents This includes acids, bases, hydrocarbons, alcohols, amines, ketones, aldehydes, esters, phosphates and their mixtures in different proportions.

Mixed aqueous–organic solvents This includes organic solvents mixed with water, mineral acids, inorganic bases or dimethyl sulfoxide and buffered salt solutions.

Complexing solvents Solutions of surfactants (sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB), Triton X-100) and ethylenediaminetetraacetic acid.

TLC with mobile phases of lower volatility gives better reproducibility compared to volatile mobile phases, although the latter have the advantage of quick evaporation from the sorbent layer after development.

Visualization

For the visualization of separated zones, physical, chemical or biological detection methods are commonly used. The physical detection methods are based on substance-specific properties and the most commonly employed methods of this group include the absorption or emission spectrophotometry, autoradiography and X-ray fluorescence. The chemical methods of detection involve spraying reagents capable of forming coloured compounds with the separated species on the plate or exposing the plate to vapour. Alternatively, the reagent can be incorporated in the mobile phase or in the adsorbent. In some cases, detection is completed by inspecting the TLC plate under ultraviolet light, after spraying with a suitable reagent, or by exposing the plate to ammonia vapour. Bioautographic analysis, reprint methods and enzymatic tests can also be applied for detection purposes. Immunostaining and flame ionization detection methods have also been reported.

The detection methods and reagents used in inorganic TLC are summarized below.

Metal Ions

In addition to using conventional detection reagents such as dithizone, dimethylglyoxime, potassium ferrocyanide and 8-hydroxyquinoline, for cations, new reagents such as sulfochlorophenol azorhodamine, phenolazotriaminorhodamine and benzolazobenzolazorhodamine have been proposed for selective detection of toxic heavy metals at nanogram levels. Radiometry is used to detect Pr(III), Pr(IV) and Tb(III). An elegant fluorescent method for the detection of Mg, Al, Ca, V, Cu, Zn, Ge, Y, Zr, Mo, Ag, Cd, In, La, Ce, Eu, Tb, Tl, Pb, and Bi at $3–3 \times 10^{-6}$ μmol levels has been reported whereby these cations are detected as coloured fluorescent zones generated simply on heating the chromatograms on porous glass sheets at 100–700°C for 15 min. Typical representative fluorescence spectra are shown in **Figure 3**.

Anions

For the detection of anions, saturated silver nitrate solution in methanol, 0.2–0.5% diphenylamine solution in 4 mol L^{-1} H_2SO_4, 1% aqueous solution of potassium ferrocyanide, 0.5% alcoholic solution of pyrogallol, 10% $FeCl_3$ solution in 2 mol L^{-1} HCl, 1% KI in 1.0 mol L^{-1} HCl and mixture of aqueous KSCN and $SnCl_2$ in 1.0 mol L^{-1} HCl, ammoniacal $AgNO_3$, aqueous bromocresol green, $FeSO_4 + FeCl_3$, alizarin, alizarin-zirconium lake, benzidine solution, $(NH_4)_2 MoO_4 + SnCl_2$ and 0.1% bromocresol purple containing dil. NH_4OH have been used. Autoradiography, scintillation counting and radiometric detection methods have also been applied. Several anions are detected on the basis of quenching effects: dark spots of the anions appeared on the bright greenish fluorescent background when the chromatograms are sprayed with aluminium(III)–morin fluorescent complex (prepared by dissolving 5 mg $AlCl_3$ and 5 mg of 2′,3,4′,5,7-pentahydroxyflavone (morin) in a mixture of 10 mL 30% CH_3COOH, 20 mL 98% ethanol and 20 mL water). The detected anions are IO_3^-, IO_4^-, CrO_4^{2-}, PO_4^{3-}, $Cr_2O_7^{2-}$, NO_2^-, NO_3^-, SO_4^{2-}, SO_3^{2-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and BrO_3^- (strong violet spots), F^-, Cl^-, Br^-, I^-, S^{2-}, $S_2O_3^{2-}$, VO_3^-, VO_4^{3-}, and MoO_4^{2-} (medium blue spots) and ClO_2^-, ClO_3^-, ClO_4^-, SCN^- and WO_4^{2-} (weak yellow spots). Several anions producing intense blue colour with

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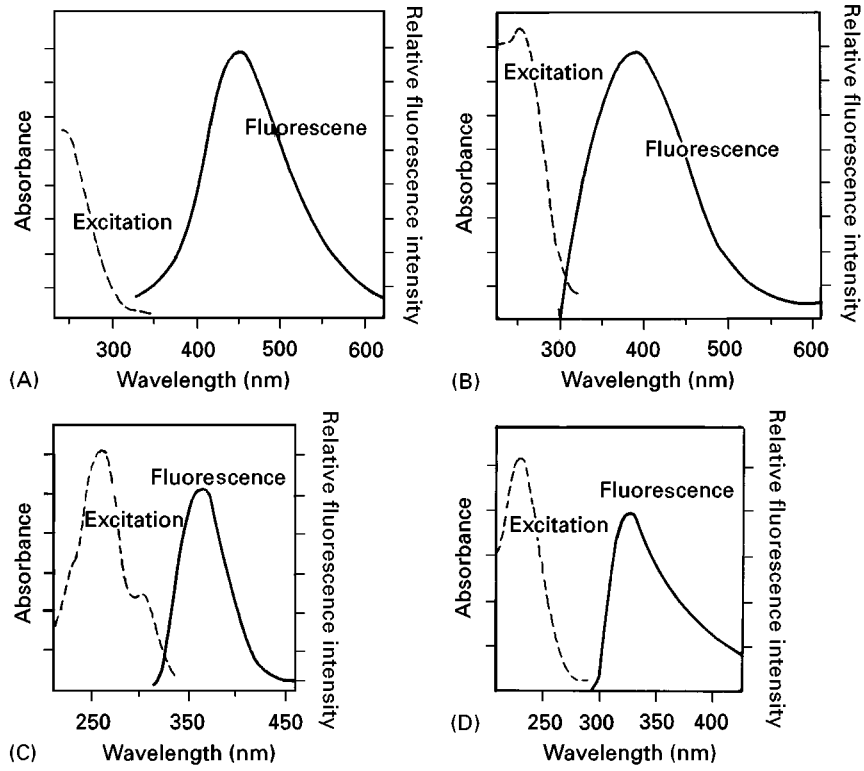

Figure 3 Fluorescence spectra of (A) copper, (B) lead, (C) cerium and (D) thallium ions heated on porous glass sheet. (Reproduced with permission from Yoshioka M *et al.* (1992) Fluorescence reactions of inorganic cations heated on a porous glass sheet for thin-layer chromatography. *Journal of Chromatography* 603: 223–229.)

0.2% Ph_2NH in H_2SO_4 are detected down to 0.1 μg on silufol layers. Halides have been detected with alizarin-zirconium lake and $AgNO_3$.

Rare Earth Elements

The REEs have been detected by first, spraying the plate with 0.1% arsenazo(III) solution and then with aqueous ammonia followed by gentle heating; second, heating at 70°C for 10 min after spraying with 0.02% chlorophosphonazo solution; and third, exposure of the plate to NH_3 after spraying with tribromochlorophosphonazo or xylenol orange solution. Saturated ethanolic solution of alizarin and dilute solutions (0.2–1%) of tribromoarsenazo have been used to detect REE.

Metal Complexes

Most of the complexes being coloured are visible without further treatment, e.g. $Fe(phen)_3^{2+}$; $Fe(bpy)_3^{2+}$; metal glyoxaldithiosemicarbazone; thiocarbonate complexes of Cu, Ni and Co; anil complexes of Cu, Mn, Fe and Zn; metal chelates of V, Co, Cr, Ni and Mn with 2,2′-dihydroxy-5,5′-dimethylazobenzene; trifluoroacetylacetonates of rate earths; metal xanthates; metal chelates of 1-hydroxyphenazine; metal diethyldithiocarbamate complexes; metal dithizonates; transition metal monothio-β-diketonates; dithioacetylacetone; metal acetothioacetanilide. Metal oxinates, some geometrical isomeric complexes of Rh, Pt and Co, methylbenzyldithiocarbonate metal chelates, Cu(II) carboxylates and Co (gly) are self-coloured but located under ultraviolet light. Trisethylenediamine Co(III) complexes are detected with sodium sulfide solution. β-Diketonates of Fe, Cr and Co, organotin compounds, alkali metal xanthates and piperidine dithiocarbamate complexes can be detected with iodine vapour. A fluorometric method has been used for the detection of heavy metal complexes with pyrene-substituted *N*-acylthiourea. Sometimes spots are detected by spraying coloured reagents such as pyrocatechol violet and copper sulfate as well as by immersing the TLC plates in a dilute solution of phenylfluorone reagent. *N*,*N*-diethyl-*N*′-benzoylthiourea-metal chelates have been detected by graphite furnace atomic absorption spectrometry and by UV detection. These techniques permit the sensitive detection of enriched platinum metals with detection limits in the nano- and picogram range (**Table 2**).

Table 2 Absolute detection limits for *N,N*-di ethyl-*N′*-benzoyl-thiourea chelates in chromatography

Element	*HPTLC* (*ng*)	*HPLC* (*ng*)	*λ* (*nm*)
Ru	0.22	10.018	275
Rh	0.21	10.006	261
Pd	0.08	10.008	274
Os	0.46	10.021	244
Ir	0.22	10.042	252
Pt	0.25	10.010	249

Data from Sehuster M (1992) Selective complexing agents for the trace enrichment of platinum metals. *Fresenius Journal of Analytical Chemistry* 342: 791–794.

Qualitative Analysis

Identification

In TLC the identification of separated compounds is primarily based on their mobility in a suitable solvent which is described by the R_F value of each compound, where:

$$R_F = \frac{\text{distance of spot migration from the origin}}{\text{distance of solvent front from origin}}$$

The factors which influence the magnitude of the R_F include the nature of the sorbent, layer thickness, activation temperature, chamber saturation, nature of the mobile phase, pH of the medium, room temperature, sample volume, relative humidity and mode of development. Another term, R_M, which is the logarithmic function of the R_F value, i.e. $R_M = \log(1/R_F - 1)$, is more useful as it bears a linear relationship to some TLC parameters or structural elements of the analyte. However, in cases of continuous and multiple development, where the solvent front is not measured, the term R_X:

$$R_X = \frac{\text{distance travelled by solute}}{\text{distance travelled by standard}}$$

is used.

If the retention data (R_F, R_M, or R_X values) of the compound to be identified are identical with those of the reference substance in three different solvent systems but on the same stationary phase or with the same solvent but on three different types of stationary phases, the two compounds can be regarded as identical with a good probability. However, for correct identification the chromatographic retention data are not enough and at least one spectroscopic method is necessary.

Table 3 hR_F ($R_F \times 100$) values, standard deviation (SD) of R_F values of metal ions present in industrial wastewater and dilution limits of metal ions in standard spiked water

Metal ion	hR_F *value*	*SD of* R_F *value*	*Detection limit* (*μg*)
Pb^{2+}	00	34×10^{-4}	7.78
Cd^{2+}	62	44×10^{-4}	6.00
Zn^{2+}	70	12.2×10^{-3}	0.46
Cu^{2+}	97	26×10^{-4}	5.23
Co^{2+}	97	12.4×10^{-3}	7.40
Ni^{2+}	97	58×10^{-4}	3.22

Stationary phase: silica gel G; mobile phase: 1.0 mol L^{-1} sodium formate + 1.0 mol L^{-1} KI (1 + 9). (Reproduced with permission from Mohammad A (1995) Identification, quantitative separation and recovery of copper from spiked water and industrial wastewater by TLC-atomic absorption and TLC-titrimetry. *Journal of Planar Chromatography – Modern TLC* 8: 463–466.)

Separation

The separated components of a mixture are detected and their R_F values recorded from the values of R_L (R_F of leading front) and R_T (R_F of trailing front). Some of the basic requirements for a good separation are (a) each spot should be compact ($R_L - R_T \leq 0.3$), (b) the difference in R_F values of two adjacent spots should be at least 0.1, (c) no complexation should occur between/among separable species and (d) chromatography of reference compounds and the

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Table 4 Separation of thorium from uranium in presence of common anions

Anions	ΔR_F	K_{Th}	α	R_S
I^-	0.50	1.22	24.40	2.56
IO_3^-	0.41	0.96	10.60	2.34
Br^-	0.51	1.27	25.40	2.62
BrO_3^-	0.40	1.00	9.09	2.22
NO_3^-	0.40	1.00	9.09	2.00
Cl^-	0.48	1.38	27.60	2.74
SCN^-	0.25	0.54	4.91	1.25
S^{2-}	0.30	0.66	6.00	1.20

ΔR_F = Difference in the R_F values of UO_2^{2+} and Th^{4+}. K_{Th} = Capacity factor of Th^{4+} [$K_{Th} = (1 - R_F)/R_F$) for thorium]. α = Separation factor ($\alpha = K_{Th}/K_{UO_2}$). R_S = Resolution for the separation of Th^{4+} from UO_2^{2+}. [$R_S = D/0.5\,(d_1 + d_2)$]: D = distance between the centres of separated spots of Th^{4+} and UO_2^{2+} whereas d_1 and d_2 are their respective diameters. Stationary phase: silica gel; mobile phase: dimethylamine–acetone–formic acid (2 + 6 + 2, v/v). Reproduced with permission from Mohammad A and Fatima N (1988) A new solvent system for the separation of Th^{4+}, UO_2^{2+} and Zr^{4+} in the presence of common anions by thin layer chromatography. *Chromatographia* 25: 536–538.

Table 5 Separation of Zn–Cd–Hg mixture in spiked environmental samples

Metal ion	R_F *values of separated ions*			
	Seawater	*Industrial wastewater*	*River water*	*Soil*
Cd^{2+}	0.79	0.81	0.81	0.80
Hg^{2+}	0.96	0.90	0.96	0.98
Zn^{2+}	0.10	0.11	0.11	0.12

Stationary phase: silica gel G impregnated with 0.1% thorium nitrate; mobile phase: 1.0 mol L^{-1} aqueous solution of sodium formate (pH 7.65). The presence of pesticides (malathion, carbaryl, carbofuran, bavistin and 2,4-dichlorophenoxy acetic acid) and anions (Cl^-, Br^-, I^-, SCN^-, MoO_4^{2-} and CrO_4^{2-}) did not hamper the separation of Zn^{2+} from Hg^{2+} and Cd^{2+}. Reproduced with permission from Mohammad A and Majid Khan MA (1992) *Proceedings of National Conference on Clean Environment Strategies, Planning and Management*. Lucknow, India, pp. 191–193. Lucknow: Legend India Environment Protection Pvt. Ltd.

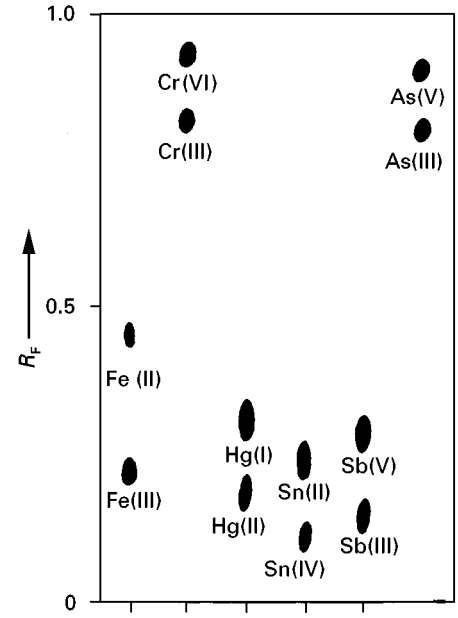

Figure 5 Chromatogram of the separation of some ions of different valency states on aminoplast layers developed with ethanol–2-propanol–5 mol L^{-1} HCl (2 : 1 : 2). (Reproduced with permission from Perisic-Janjic NU, Petrovic SM and Podunavac S (1991) Thin-layer chromatography of metal ions on a new carbamide–formaldehyde polymer. *Chromatographia* 31: 281–284.)

mixture should be performed under identical experimental conditions. Selected examples of TLC/HPTLC separation of inorganic ions are given in **Tables 3–5** and **Figures 4–10**. Bonded silica C_{18} reversed-phase layers in combination with a methanol–lactate medium as mobile phase have been found to be most suitable for the separation of adjacent rare earths of middle atomic weight group (Figure 4). Carbamide–formaldehyde polymer (aminoplast) with acidic eluents is useful for the separation of metal ions of different valency states (Figure 5). Figures 6 and 7 show the separation of

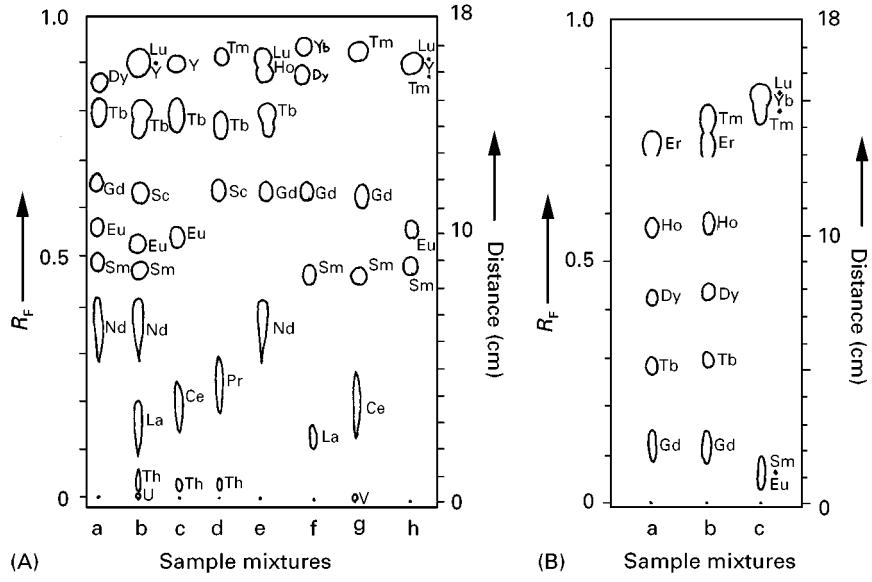

Figure 4 TLC separation of rare earth element on C_{18}-bonded silica with eluent systems (A) 1.0 mol L^{-1} lactate in 50% methanol (pH adjusted to 6.35 before mixing with methanol) and (B) 0.5 mol L^{-1} lactate in 50% methanol (pH adjusted to 6.35 before mixing with methanol). (Reproduced with permission from Kuroda R, Adachi M and Oguma K (1998) Reversed-phase thin-layer chromatography of rare earth elements. *Chromatographia* 25: 989–992.)

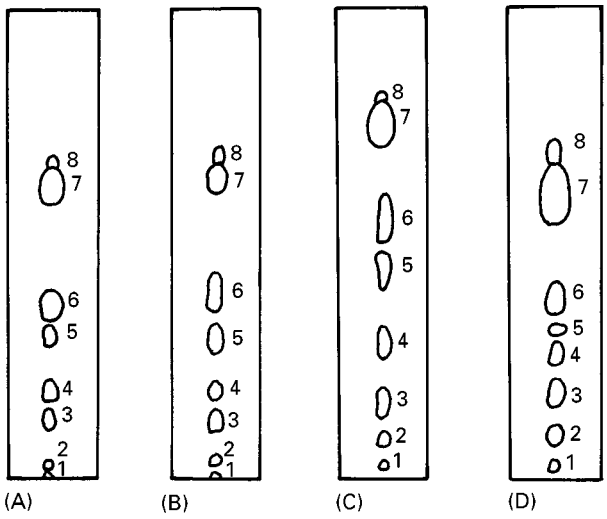

Figure 6 Separation of a mixture of diantipyrilmethane (DAM) salts. Mobile phase: acetone–chloroform (3 : 1 v/v). Reagents: (A) DAM; (B) MDAM (C) HDAM; (D) PDAM. Anions: 1, SO_4^{2-}; 2, Cl^-; 3, Br^- ; 4, NO_3^-; 5, SCN^-; 6, I^-; 7, ClO_4^-; 8, reagent. (Reproduced with permission from Shadrin O, Zhivopistsev V and Timerbaev A (1993) Thin-layer chromatographic determination of inorganic anions as counter-ions of metal diantipyrilmethane cationic complexes and diantipyrilmethane cations. *Chromatographia* 35: 667–670.)

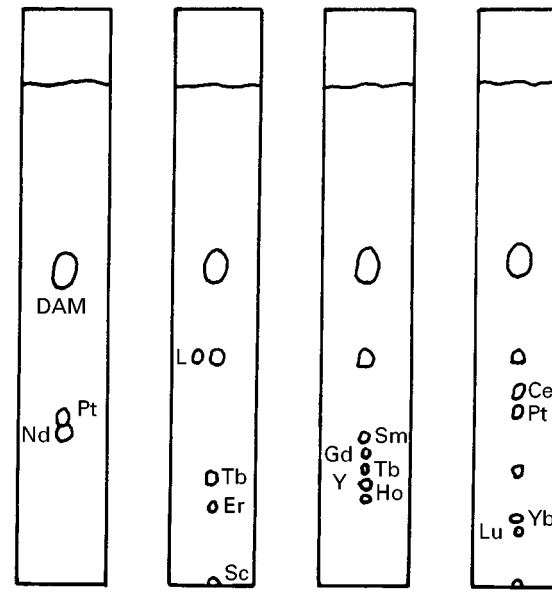

Figure 8 Separation of the mixture of diantipyril methanates of rare earth elements. TLC plate: silufol; mobile phase: *n*-propanol–0.7 mol L^{-1} HCl (9 : 2). (Reproduced with permission from Timerbaev A, Shadrin O and Zhivopistsev V (1990) Diantipyrilmethane as complex-forming reagents in the thin-layer chromatographic determination of metals. *Chromatographia* 30: 436–441.)

common anions in the form of metal diantipyrilmethane (DAM) complexes and salts of protonated DAM. The separation takes place on silica gel plates with elution by organic solvent–mineral acid or binary organic solvent mixtures using ascending or radial development. Being highly coloured (iron complexes) or fluorescent under ultraviolet light (terbium complexes), chromatographic zones can easily be detected. Mixtures of REEs as diantipyrilmethanates are well resolved on silufol plates (Figure 8). A four-component mixture consisting of 4-methyl-2-pentanone, tetrahydrofuran, nitric acid and mono-2-ethylhexyl ester of 2-ethylhexylphosphoric acid (P 507) has been used for HPTLC resolution of 10 rare earths (Figure 9). HPTLC allows fast and effective separation of platinum group metals with *N*,*N*-diethyl-*N*′-4-(1-pyrene)butyrylthiourea (DE Py BuT) on silica gel layers using toluene as the mobile phase (Figure 10).

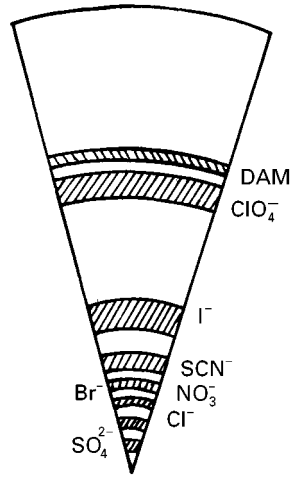

Figure 7 Sector of the radial thin-layer chromatogram of the mixture of diantipyrilmethane (DAM) salts. (Reproduced with permission from Shadrin O, Zhivopistsev V and Timerbaev A (1993) Thin-layer chromatographic determination of inorganic anions as counter-ions of metal diantipyrilmethane cationic complexes and diantipyrilmethane cations. *Chromatographia* 35: 667–670.)

Quantitative Analysis

Methods for the quantitative evaluation of thin-layer chromatograms may be divided into two main categories: quantitation after elution from the layer and *in situ* quantitation on the layer. In the first, quantitation is performed after scraping off the separated analyte zone, collecting the sorbent and recovery of the substance by elution from the sorbent. Thereafter, the eluates are analysed by applying any suitable method of analysis, such as GC,

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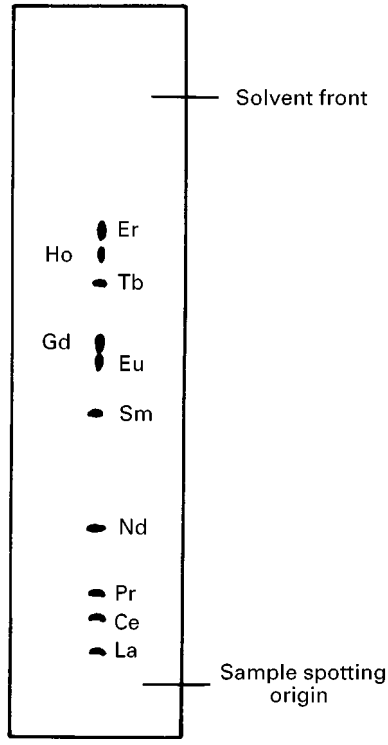

Figure 9 Chromatogram of the 10 rare earths using optimum mobile-phase conditions: 4-methyl–2-pentanone–THF–HNO_3–P 507 (3 : 1.5 : 0.46 : 0.46). (Reproduced with permission from Wang QS and Fan DP (1991) Optimization of separation of rare earths in high-performance thin-layer chromatography. *Journal of Chromatography* 587: 359–363.)

spectrophotometry or titrimetry. In the second, solutes are assayed directly on the layer with the help of visual, manual or instrumental measurement methods.

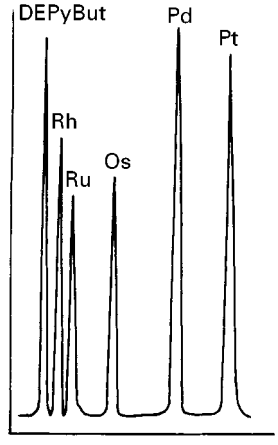

Figure 10 HPTLC separation of platinum group metals with DEP_Y BuT. Eluent: toluene; relative humidity 5.0%, separation distance, 6 cm (Reproduced with permission from Schuster M and Unterreitmaier E (1993) Fluorometric detection of heavy metals with pyrene substituted *N*-acylthioureas. *Fresenius Journal of Analytical Chemistry* 346: 630–633.)

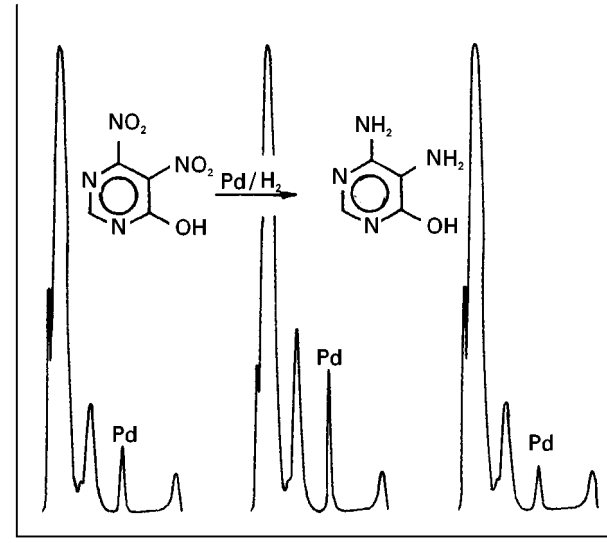

Figure 11 HPTLC determination of Pd in a synthesis solution. Ligand: *N,N*-di-*n*-hexyl-*N′*-benzoylthiourea. Stationary phase: silica gel 60, mobile phase: chloroform, relative humidity: 20%, separation distance: 3 cm detection: reflectance at 280 nm. (Reproduced with permission from Schuster M (1992) Selective complexing agents for the trace enrichment of platinum metals. *Fresenius Journal of Analytical Chemistry* 342: 791–794.)

In situ densitometry, a preferred technique for quantitative TLC, involves the measurement of visible or ultraviolet absorbance, fluorescence of fluorescence quenching directly on the layer. The measurements are made either through the plates (transmission), by reflection from the plate, or by reflection and transmission simultaneously, using either single-beam, double-beam, or single-beam–dual-wavelength

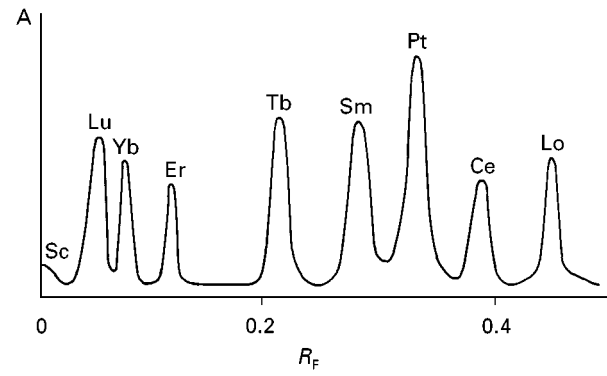

Figure 12 Densitogram of a mixture of rare earth element complexes. Stationary phase: silufol, mobile phase: *n*-propanol–0.7 mol L^{-1} HCl (9 : 2): spraying reagent: 0.1% arsenazo III; wavelength: 590 nm. (Reproduced with permission from Timerbaev A, Shadrin O and Zhivopistsev V (1990) Diantipyrilmethane as complex-forming reagents in the thin-layer chromatographic determination of metals. *Chromatographia* 30: 436–441.)

Table 6 Quantitative and semiquantitative determination methods for inorganic ions

Method	*Species determined*
TLC-densitometry	B, Pb, Fe, Cu, Mn, Co, Ni, Mg, Zr, Mo, Ba, La, Ce, Sr, Se, Tl, Hg, phosphates, selenocyanate, U, Cd, Y, NO_2^-, NO_3^-, $Fe(CN)_6^{3-}$, SCN^-, rare earth elements, Co(III)-1-(2-pyridylazo)-2-naphthol complex and bis carboxy ethyl germanium sesquioxide
TLC-spectrophotometry	Pb, Zn, Ni, Cu, Co, Zr, Pd, Mo, U, Hg(II), metal complexes, SCN^-, La, Ce, Pr, Nd, Cr(III), Fe(II), $Cr_2O_7^{2-}$ and $Fe(CN)_6^{3-}$
TLC-UV spectroscopy	Hg(II), Cu, Cd
TLC-titrimetry	Cu, SCN^-
TLC-atomic absorption spectroscopy (AAS)	Cu, Zn, Fe, Ni, Pb, Mn
ICP-TLC-atomic emission spectrometry (AES)	Rare earth elements, heavy metals
Neutron activation-circular TLC	Rare earth elements
Square wave-stripping voltammetry-TLC	Pb, Cd, Zn, Cu
TLC-photoacoustic measurement	Cobalt complex of 1-(2-pyridylazo)-2-naphthol
TLC-emission spectrometry	Alkaline earth metals
Visual colorimetry and peak spot-area measurement	Ti, Ni, Cu, Cr, Pb, Ag, Th, Tl(I), Al, Co, Zr, Fe(II), Fe(III), V, U, Cd, Zn, Ce, Hg, IO_4^-, Br^-, I^-, NO_2^-, Cl^-, NO_3^-, SCN^-, SO_4^{2-}, BrO_3^-

Source: *Chemical Abstracts* (1973–1996), USA.

scanning instruments. Modern optical densitometric scanners are linked to a computer and are capable of automated peak location, multiple wavelength scanning and spectral comparison of fractions in several operating modes (reflectance, absorption, transmission and fluorescence). Representative examples of HPTLC determination and densitometry are shown in **Figures 11** and **12**.

The combination of TLC with other analytical techniques has proved useful for the analysis of complex samples. Spectrophotometry, HPLC, inductively coupled plasma–mass spectrometry and voltammetry in conjugation with TLC are the most commonly used techniques. However, infrared, thermal anlaysis and mass spectrometry have also been used.

For semiquantitative analysis, visual comparison and spot-size measurement methods are used. A definite volume of sample is chromatographed alongside standards containing the analyte. After detection, the amount of analyte in the sample is estimated by visual comparison of the size and intensity of the sample zone with the standards. This method works

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Table 7 TLC results of the determination of Ti, Zr, Hf, La and Tb in various samples

Technique	*Sample*	*Analyte*	*Determination results*	
			Amount found (mean and SD)	*Known amount (concentration)*
Spot-area measurement method	Sulfite-cellulose liquor	Ti	31 ± 4 p.p.m.	35 p.p.m.
	High speed steel	Ti	25 ± 3 mg g^{-1}	29.3 mg g^{-1}
TLC-spectrophotometry	Synthetic mixture (Zr + Hf)	Zr	10.4 ± 0.3 μg	10 μg
		Hf	9.7 ± 0.2 μg	10 μg
	Mg–Al–Zr–Hf	Zr	1.1 ± 0.2 mg g^{-1}	1.1 mg g^{-1}
TLC-densitometry	Synthetic mixture	La	1.1 ± 0.1 μg	1.2 μg
		Tb	1.4 ± 0.1 μg	1.6 μg
	Lanthanum glass	La	179 ± 5 mg g^{-1}	174 mg
		Tb		
	Monazite	La	4.0 ± 0.2 mg g^{-1}	4.3 mg g^{-1}
		Tb	1.1 ± 0.2 mg g^{-1}	1.2 mg g^{-1}

Reproduced with permission from Timerbaev A, Shadrin O and Zhivopistsev V (1990) Diantipyrilmethane as complex-forming reagent in the thin layer chromatographic determination of metals. *Chromatographia* 30: 436–441.

Table 8 Comparison of results of anions in water samples by TLC and ion chromatography (IC)

Sample	*Technique*	*Determination results* (*p.p.m.*)		
		SO_4^{2-}	Cl^-	NO_3^-
Ground water	TLC	34 ± 5	ND	10 ± 2
	IC	38.3	ND	12.8
Lake water	TLC	25 ± 4	29 ± 5	ND
	IC	27.2	28.0	ND
River water	TLC	9.8 ± 1.6	6.3 ± 1.2	ND
	IC	9.3	7.0	2.9

ND, not detected. Reproduced with permission from Shadrin O, Zhivopistsev V and Timerbaev A (1993) Thin-layer chromatographic determination of inorganic anions as counter-ions of metal-diantipyrilmethane cationic complexes and diantipyrilmethane cations. *Chromatographia* 35: 667–670.

well if the applied amounts of sample are kept close to the detection limit and the sample is accurately bracketed with standards. The shape and size of the spot produced are significantly influenced by the amount of analyte. A linear relationship between the size of the spot and the amount of analyte has been observed. This method has been used for semiquantitative estimation of titanium in steel and inorganic anions in water.

TLC techniques used and the species determined are listed in **Table 6**. TLC results of determination of certain species in real samples are shown in **Tables 7** and **8**, which indicate the versatility and accuracy of TLC.

Application

Some applications of inorganic TLC have been covered above. **Tables 9–11** list representative applications of TLC as used for the analysis of anionic, cationic and metal complex mixtures. In **Table 12** selective TLC applications related to the analysis of real samples (biological, food, geological, industrial, pharamaceutical, soil, water, wastewater and irradiated products) have been given.

Further Developments

Looking to the future, it is reasonable to expect increasing use of TLC and HPTLC for more application-oriented research in several fields (pharmaceutical, environmental, geological, forensic, agrochemical, textile, cosmetic and food sciences) because of the continued development of computer and microprocessor-based instrumental TLC. Layers with immobilized phases of wider range of selectivity, automation of sample application, hybrid mobile phases with improved chromatographic performance, online

Table 9 Stationary and mobile phases used in the analysis of certain anionic species

Anions	*Stationary phase*	*Mobile phase*
Hexacyanoferrate (II) and (III)	Silica gel G, alumina G	Polyhydric alcohols, formamide, DMF, methylamine, pyridine, water, ketones, esters and their mixtures in various ratios
Sulfur oxyanions	Silufol UV 254	Ethanol–dioxane–water–NH_4OH (30 + 60 + 50 + 25)
Oxyanions	Cellulose, microcrystalline cellulose containing fluorescent indicator	28% Aqueous ammonia–acetone–*n*-butanol (6 + 13 + 3), 28% aqueous ammonia–acetone (2 + 3), dioxane–water (3 + 2), acetone–acetic acid–water (20 + 1 + 20)
Halogen anions	Silica gel G, zirconium(IV) molybdate, cellulose	Basic and polar solvent systems, various alcohols mixed with aqueous ammonia
Phosphorous anions	Cellulose	Water–ethanol–2-methylpropanol–2-propanol–aqueous ammonia–trichloroacetic acid (150 + 175 + 75 + 107 + 2 + 25)
Arsenate, arsenite	Aluminium oxide	Aqueous solutions of KNO_3, Na_2CO_3, NaOAc, HOAc, K_2SO_4, K_3PO_4, NaF, acids and bases and buffer solutions
Oxyanions, chromate, dichromate, oxalate	Silica gel G impregnated with 0.1% aq. solutions of $CuSO_4$, $ZnSO_4$, $NiCl_2$, $CoCl_2$, $Co(NH_3)_6Cl$	Acetone–DMSO or formic acid, acetone–DMSO–formic acid and acetone–mineral acid mixtures

DMF, dimethylformamide; DMSO, dimethylsulfoxide.

Table 10 Stationary and mobile phases used in the analysis of some cationic species

Metal ions	*Stationary phase*	*Mobile phase*
Alkali and alkaline metals	Microcrystalline cellulose, cellulose (MN-300) microcrystalline cellulose Lk, zinc ferrocyanide, tin(IV) arsenosilicate and arsenophosphate	Methanol–conc.HCl–water (8 + 1 + 1, 7 + 1 + 2), dioxane–2-propanol–conc. HCl–H_2O (7 + 7 + 5 + 8). HNO_3–methanol mixtures, buffered EDTA solutions, aqueous ammonium nitrate
Transition metals	Silica gel G, DEAE cellulose in chloride form, chitosan, chitin, silica gel impregnated with high molecular weight amines, cellulose	Aqueous solutions of HCl (1–5 mol L^{-1}), LiCl (1–9 mol L^{-1}), $MgCl_2$ (2.5 mol L^{-1}), $CaCl_2$ (2.5 mol L^{-1}) and saturated NaCl, Me_2CO–EtOAc–C_6H_6 (7 + 1 + 3), 0.03 mol L^{-1} citric acid, HNO_3 at different concentrations
Light rare earth metals	Mixture of silica gel, starch and NH_4NO_3; silica gel–NH_4NO_3–CM cellulose (5 : 0.64 : 0.16, w/w)	P_{204}-dioxane–EtOAc–HNO_3(1.1 + 2 + 2.4 + 4) tributylphosphate–THF–diethyl ether–HNO_3 (1 + 9 + 9 + 1.5), trialkylmethyl ammonium chloride–*n*–octyl alcohol–petroleum ether–conc. HNO_3 (60 + 7 + 25 + 1)
Heavy rare earth metals	Silica gel–NH_4NO_3–CM-cellulose (5.0 + 0.64 + 0.16, w/w); silica gel–starch–ammonium rhodanate (2.8 + 0.15 + 0.5, w/w)	Et_2O–THF–bis (2–ethylhexyl)phosphate–HNO_3, trimethylammonium chloride–*n*-octyl alcohol–petroleum ether–HCl (2 + 10 + 30 + 1, 2 + 6 + 30 + 1.2 and 2 + 7 + 30 + 1), bis (2 + ethylhexyl)phosphate–diisopropyl ether–diethyl ether–nitric acid (1 + 10 + 6 + 1.1), mono(2-ethylhexyl) phosphate–isopropyl ether–diethyl ether–nitric acid (1 + 8 + 8 + 1.1)
Lanthanides	Silanized silica gel (Merck) and polygram plate, silica gel impregnated with different concentrations of mono (2-ethyl hexyl) phosphate	3 mol L^{-1} Tributyl phosphate in HNO_3–isooctane (2 + 8); THF–paraldehyde–HNO_3 (2 + 7 + 1); 0.3 mol L^{-1} triphenylphosphine oxide in paraldehyde–HNO_3 (9 + 1); di-isopropyl ether–THF–HNO_3 (10 + 6 + 1); HNO_3 (0.05–3.0 mol L^{-1})
Radionuclides ^{90}Sr, ^{90}Y, ^{140}Ba, ^{140}La	Silica gel (with and without gypsum binder)	Aqueous solutions of NaCl, KCl, NH_4Cl, $CaCl_2$, $SrCl_2$, and $BaCl_2$
High valence metal ions	Silica gel impregnated with crystalline antimonic(V) acid-*p*-sulfochlorophosphanazo	Potassium pyrophosphate solution
Mn(II), Mn(III)	Silica gel G	Eleven organic mobile phases consisting of hydrocarbons and their derivatives in different ratios
Transition metals	1,10-Phenanthroline (1%), DMG (1%), EDTA (2%) or β-naphthol (0.1%) impregnated silica gel	Pyridine–benzene–HOAc–H_2O (6 + 5 + 8 + 4), BuOH–benzene–formic acid (5 + 10 + 9), pyridine–benzene–HOAc–H_2O (5 + 5 + 4 + 1)

DEAE, diethylaminoethyl; THF, tetrahydrofuran; DMG, dimethylglyoxime; EDTA, ethylenediaminetetraacetic acid.

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coupling of TLC with other sensitive techniques, better approaches in method development and application of detection reagents and greater use of instrumental densitometry can be expected. It is hoped that the forced-flow layer methods with increased automation will be developed in the near future for faster separation of inorganic ions in real samples.

Table 11 Stationary and mobile phases used in the analysis of certain metal complexes

Metal complexes	*Stationary phase*	*Mobile phase*
Diethylthiocarbamates of Bi, Cu, Co, Ni	Silica gel G	Dichloromethane–petroleum ether (5 + 3)
Sulfate complexes of Pt, Pd, Rh, Ir	Commercial silufol plates (Kavalier, CSSR), silica gel KSK, silica gel	0.1, 1.0 and 6.0 NH_4SO_4, 0.2 or 0.5 mol L^{-1} tetraoctylamine in benzene
β-Diketonates of Fe, Cr and Co	Silica gel (Merck)	CCl_4, toluene, benzene, dichloromethane, diethyl ether
Xanthates of Cu, Ni, Co, Mo, Bi, Pb, Zn	Silica gel G	CCl_4–$CHCl_3$ (10 + 1), toluene–benzene (10 + 1)
Anil complexes of Mn, Fe, Cu, Zn	Silica gel–starch (19 : 1)	Acetonitrile, methanol, ethanol, butanol, acetic acid or butanol–acetic acid (4 + 1, 3 + 2, 2 + 3, 1 + 4)
Metal oxinates (OX), (HOX), Cu $(OX)_2$, Zn $(OX)_2$, $Al(OX)_3$, $Ga(OX)_3$, In $(OX)_3$	Styragel 60A (polystyrene–divinylbenzene copolymers), Merckogel OR-PVA 2000	$CHCl_3$, *p*-dioxane, benzene, 10^{-3}–10^{-1} mol L^{-1} HOX in $CHCl_3$, 10^{-2} mol L^{-1} HOX in dioxane, 10^{-1} mol L^{-1} pyridine in $CHCl_3$
Mn, Co, Ni, Zn, Rh, Pd, Pt, Chelates of dithioacetylacetone	Silica gel	CCl_4, 1,1,1-trichloroethane
Mixed amino carboxylato cobalt(III) complexes	Polyacrylonitrile	Aqueous ammonium sulfate solutions (1.1–3.48 mol dm^{-3})
Chlorosulfate complexes of transition metals and rare earths	Silica gel G–cellulose (2 : 1)	Sodium formate (1 mol L^{-1}) and ammonium sulfate (1 mol L^{-1})
Mercapto-4-methyl-5-phenylazopyrimidine complexes of Co, Ni, Pb, Cd, Cu	Surfactant-impregnated silica gel plate	Acetonitrile–xylene (70 : 30)

Table 12 Application of TLC to the analysis of real samples

Species	*Sample*	*Remark*
Se	Biological (tissues, blood, serum) environmental (drinking and surface water) and food stuffs	Isolation of Se from matrix, derivatization, extraction of Se-contaning complex, TLC separation and fluorimetric determination. Detection limit 250 fg Se per spot
Cu, Fe	Serum	TLC separation and densitometric determination of Fe^{2+}, Fe^{3+} and Cu^{2+} complexed with 2-[(5-bromo-2-pyridinyl)azo]-5-(diethylamino) phenol in serum
Cd, Hg, Pb	Urine, blood	Separation on silica gel layer prior to spectrophotometric determination of Cd^{2+}, Pb^{2+} and Hg^{2+} in blood and urine samples
Heavy metals	Urine, blood, excrement	A sensitive detection of Zn^{2+}, Hg^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Ag^{+} and Bi^{3+} on silica gel layers (sensitivity 10^{-3} g L^{-1}) as dithizonates in biological samples
Hg	Animal, fish and plant tissues	Quantitative determination of mercury species (inorganic and methyl mercury) after extraction from tissues
Cu, Mg, Zn, Fe, Mn	Human faeces	Detection of metal–EDTA complexes on silica gel and cellulose layers
BrO_3^-	Food stuff	Extraction and purification using alumina column, separation on silica gel layer and densitometric determination of BrO_3^- in bread and flour dough. Detection limit of BrO_3^- was 0.1 μg g^{-1} of bread
Fe, Mn, Co	Human milk	Extraction of metals from human milk with isobutyl methyl ketone–amyl acetate (2 : 1) and identification on cellulose layer

Table 12 *Continued*

Species	*Sample*	*Remark*
Polyphosphoric acids	Cheese, milk	Extraction with 25% trichloroacetic acid, separation and identification on polyamide layer developed with *n*-butanol–formic acid (1 : 1)
Polyphosphates	Soft drinks	Separation and determination of ortho- and polyphosphates in soft drinks using two-dimensional TLC and ion-exchange column chromatography
Si	Edible oils	Detection with rhodanine on silica gel layers developed with light petroleum–diethyl ether (98 : 2)
Rare earth metals	Rocks, monazite sand, ores, irradiated nuclear fuels	Determination by neutron activation analysis (determination limits 0.05–10 $\mu g\, g^{-1}$ for 10–30 mg sample) after preconcentration by circular TLC on Fixion 50 × 8. Use of ICP-AES for determination of rare earths in concentrates obtained by means of TLC. Densitometric determination in monazite sand (linear range 0.015–0.60 μg of individual rare earth) after TLC separation. The limits of detection for rare earths were 9–12 ng
Fe, Mn, Cu	Cotton materials	Detection of metal ions on microcrystalic cellulose plates developed with acetone–HCl–H_2O (8 : 1 : 2). TLC-spectrophotometry for determination of Mn traces in textile materials
NO_3^-, $Fe(CN)_6^{3-}$	Molasses	TLC separation on silufol 254 plates developed with propanol–ammonia solution (2 : 1), detection with acidified diphenylamine and densitometric determination
La, Y	Alloys	Circular TLC with trioctylamine-treated cellulose layers as stationary phase and aqueous HCl as mobile phase for separation and spectrophotometric determination of La and Y (0.01–1.0%) in Mo-based alloys
Co	White wine	Fixation of Co^{2+} as 1-(2-pyridylazo)-2-naphthol complex on membrane filter followed by densitometric determination (concentration range in white wine 2.5–4.5 $\mu g\, L^{-1}$) by reflection absorbance of the complex
Fe(II)	Pharmaceuticals	Separation on microcrystalline cellulose layers, detection by 1,10-phenanthroline and determination by spectrophotometry
Mercury salts	Homeopathic drugs	Identification of chloride, nitrate, cyanide, sulfate and sulfide of Hg on silica gel G plates developed with acetone–chloroform–conc. HNO_3 (4 : 5 : 1)
Mn	Pharmaceuticals	TLC separation and photodensitometric determination of Mn in vitamins and pharmaceuticals as PAN complex
Cr	$Na_2^{51}CrO_4$ injection	Determination of radiochemical purity of $Na_2^{51}CrO_4$ injections and γ-scintillation for quantitation of Cr-containing zones
NO_3^-	Feeds	Separation on alumina layer and spectrophotometric determination at 430 nm after extracting the coloured product formed with 3,4-xylenol
Rare earths and fission products	Irradiated nuclear fuels	Two-dimensional TLC separation and enrichment followed by quantification by γ-spectroscopy

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Table 12 *Continued*

Species	*Sample*	*Remark*
Co, Fe(III)	Cosmic dust	TLC separation and semiquantitative determination on the basis of spot size and colour intensity or by reflectance densitometry
^{89}Sr, ^{90}Sr	Soil	Extraction of strontium from soil with dicyclohexano-18-crown-6 in chloroform and TLC separation using circular procedure with silufol layer
Ta	Molybdenum-based alloys	TLC-AES for determination of Ta ($\geq 0.5\%$) in molybdenum alloys
Zn, Pb, Cu, Cd, Hg (organic and inorganic)	Plants	Detection (10–500 ng) using azo rhodanines as detector and nanogram determination by visual sorption-photometric method
Hg (organic and inorganic)	Water	HPTLC separation on silica gel layers and densitometric determination as dithizonates
Al, Be, Cr, Bi, Cu, Hg	Water	Extraction, TLC separation, detection (as Bi, Cu, Hg dithizonates, detection limit, 0.5 p.p.m.) and determination fluorimetrically (Al and Be as oxinates) and photometrically (Cr as diphenylcarbamide complex)
$CuSO_4$, $CdSO_4$, $HgCl_2$, $AgNO_3$	Fresh and seawater	Evaporation, precipitation, micro-TLC separation and enzymatic detection
Fe, Cu, Hg, Cd, Co, Ni, Bi, Mn, Pb, Zn, Sn, Al, Cr, Be	Water	Extraction, TLC separation on silica gel layer developed with EtOH–1.0 mol L^{-1} HNO_3 (99 : 1) and photometry in transmission mode. Detection limits 0.1–1 p.p.m. except Cr (8 p.p.m.)
Cu, Zn, Cr, Fe, Ni, Co, V	Electroplating wastewater	Simultaneous separation of metals and semiquantitative determination of Ni, Cu, Cr in wastewaters using cellulose with azopyrocatechol groups as layer material. Detection limit of metals in coloured zone was 0.05–2.0 μg
Co, Ni, Cu, Fe	Industrial and wastewaters	Visual semiquantitative determination of concentration of total heavy metals in wastewaters according to the intensity of coloured metal diethyldithiocarbamates formed directly on silufol plates. Determination of Cu and Ni at 5 mg L^{-1} in electroplating wastewater
Cu, Ni, Fe, Co	Electroplating wastewater	Quantitative trace analysis using 2-(-5-bromo-2-pyridylazo)-5-diethyl aminophenol as complexing agent

EDTA, ethylenediaminetetraacetic acid; ICP-AES, inductively coupled plasma–atomic emission spectroscopy; PAN, 1-(2-pyridylazo)-2-naphthol.

See also: **II/Chromatography: Thin-Layer (Planar):** Densitometry and Image Analysis; Layers; Spray Reagents. **III/Impregnation Techniques: Thin-Layer (Planar) Chromatography. Ion Analysis:** Capillary Electrophoresis; High-Speed Counter Current Chromatography; Liquid Chromatography.

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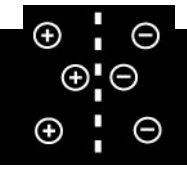
ION EXCHANGE RESINS: CHARACTERIZATION OF



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Introduction

An ion exchange resin is an insoluble polymer matrix containing labile ions which are capable of exchanging with ions in the surrounding medium without any major physical change taking place in its structure. They are of two basic types, cation and anion exchangers. So-called cation exchange resins are in fact polymeric anions to which the labile cation is bound, and it is this cation which exchanges with other cations in solution. Likewise, anion exchange resins are polymeric cations with a labile, exchangeable anion.

The first synthetic ion exchange resins were developed by Adams and Holmes in 1935, based on a phenol-formaldehyde structure. The next most important development was the introduction of commercial ion exchange resins based on a cross-linked polystyrene matrix, and these resin types today still represent about 90% of the commercial resin market. More recently, polyacrylic resins have been introduced which have widened the scope and versatility of the synthetic ion exchange resins, and these represent most of the remaining 10% of the commercial market.

The development of synthetic polystyrene and polyacrylic resins has enabled these ion exchangers to be produced in spherical bead form, unlike the irregular-shaped particles of the phenol-formaldehyde types. In the majority of applications, the most efficient treatment of a solution is obtained by passing this solution through a bed of ion exchange resin. A spherical bead shape offers optimum contact with the percolating solution without undue pressure drop across the bed, requiring only minimal inlet pressures.

The first polystyrene resins, introduced in 1947, were of what is now known as a *gel* type. Exchange takes place by diffusion of the ions through the resin structure to and from the ion exchange sites. The polymer chains are only separated by molecular distances, and the ease of penetration of the ions is very much influenced by the amount by which the resin structure can be swelled by the contacting solution. In 1956, Mikes and co-workers discovered a means of introducing pores (or holes) into the resin structure, which led to the introduction of *macroporous* resins, which further increased the scope of ion exchange techniques. These resins comprise a continuous polymer matrix interspersed with a continuous pore matrix.

DropBooks

Synthesis

Polymerization

Generally speaking, the synthesis of a modern ion exchange resin is a two-step process. In the first step, the spherical bead is produced by polymerization of styrene (or an acrylic monomer, usually methyl acrylate) plus a cross-linking agent (usually divinylbenzene, DVB) in an aqueous suspension. This technique of suspension polymerization is used extensively in the production of pearl (or bead) polymers, not specifically to make ion exchange resins, and is